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Seasonal cycle of seawater bromoform and dibromomethane concentrations in a coastal bay on the western Antarctic Peninsula

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[1] Sea-to-air emissions of bromocarbon gases are known to play an important role in atmospheric ozone depletion. In this study, seawater concentrations of bromoform (CHBr_3) and dibromomethane (CH_2Br_2) were measured regularly between February 2005 and March 2007 at the Rothera Oceanographic and Biological Time Series (RaTS) site located in Marguerite Bay on the Antarctic Peninsula. Strong seasonality in CHBr_3 and CH_2Br_2 concentrations was observed. The highest bromocarbon concentrations (up to 276.4 ± 13.0 pmol $\text{CHBr}_3 \text{ L}^{-1}$ and 30.0 ± 0.4 pmol $\text{CH}_2\text{Br}_2 \text{ L}^{-1}$) were found to coincide with the annual microalgal bloom during the austral summer, with lower concentrations (up to 39.5 pmol $\text{CHBr}_3 \text{ L}^{-1}$ and 9.6 ± 0.6 pmol $\text{CH}_2\text{Br}_2 \text{ L}^{-1}$) measured under the winter fast ice. The timing of the initial increase in bromocarbon concentrations was related to the sea-ice retreat and onset of the microalgal bloom. Observed seasonal variability in $\text{CH}_2\text{Br}_2/\text{CHBr}_3$ suggests that this relationship may be of use in resolving bromocarbon source regions. Mainly positive saturation anomalies calculated for both the 2005/2006 and 2006/2007 summers suggest that the bay was a source of CHBr_3 and CH_2Br_2 to the atmosphere. Estimates of bromocarbon sea-to-air flux rates from Marguerite Bay during ice-free periods are 84 (-13 to 275) $\text{CHBr}_3 \text{ nmol m}^{-2} \text{ d}^{-1}$ and 21 (2 to 70) $\text{nmol CH}_2\text{Br}_2 \text{ m}^{-2} \text{ d}^{-1}$. If these flux rates are representative of the seasonal ice edge zone bloom which occurs each year over large areas of the Southern Ocean during the austral summer, sea-to-air bromocarbon emissions could have an important impact on the chemistry of the Antarctic atmosphere.

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1. Introduction

[2] Volatile bromocarbon compounds such as bromoform (CHBr_3) and dibromomethane (CH_2Br_2) are known to be produced naturally in seawater [Carpenter and Liss, 2000; Quack and Wallace, 2003]. Sea-to-air flux of bromocarbons and their subsequent photodissociation in the atmosphere results in the formation of reactive radical species (BrOx) which contribute to catalytic ozone depletion in the troposphere [Platt and Honninger, 2003] and lower stratosphere [Nielsen and Douglass, 2001]. Ozone loss resulting from bromine chemistry has been estimated to be up to 30% [von Glasow et al., 2004; Yang et al., 2005]. However, there is

still considerable uncertainty surrounding the sources of bromine to the atmosphere and this remains a major limitation in atmospheric models of this element [Yang et al., 2005]. Estimates of the importance of bromocarbon compounds to atmospheric chemistry have focused on CHBr_3 and have been calculated using two different approaches. Top down estimates of CHBr_3 marine emissions to the atmosphere are based on “background” atmospheric concentrations and lifetimes, and have so far suggested a global source strength of 210 to 500 Gg $\text{CHBr}_3 \text{ a}^{-1}$ [Nielsen and Douglass, 2001]. The second approach involves global extrapolation of measured ocean saturation data and has produced a wide range of sea-to-air flux estimates (240 – 1760 Gg $\text{CHBr}_3 \text{ a}^{-1}$) [Liss, 1986; Fogelqvist and Krysell, 1991; Quack and Wallace, 2003]. Previous measurements in seawater and the marine atmosphere have suggested that the bromocarbons have highly localized emissions [Carpenter and Liss, 2000; Yokouchi, 2005; Butler et al., 2007] which could contribute significantly to the bromine inventory of the atmosphere. However, neither the “top down” nor saturation extrapolation methods for estimating sea-to-air bromocarbon fluxes

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are likely to represent strong local sources [Warwick *et al.*, 2006] since both techniques smooth limited data sets over large temporal and spatial scales. A greater understanding of variability in bromocarbon emissions to the atmosphere will help to improve source strength estimates, and our understanding of the impact of localized sea-to-air fluxes of bromine.

[3] Previous measurements and our current knowledge of bromocarbon production processes in seawater suggest that the sea-to-air fluxes of these compounds will vary geographically and seasonally. For example, Quack and Wallace [2003] present a compilation of CHBr_3 measurements in seawater which shows that coastal and shelf concentrations can be up to 100 times higher than in the open ocean. Additionally, seasonality in bromocarbon production in the marine environment has been reported in the literature. Carpenter *et al.* [2005] measured atmospheric CHBr_3 concentrations during a 2.5-year period at Mace Head, Ireland and found maxima in the mixing ratios from spring until autumn with a winter minimum. Given that the major bromocarbon source in the marine environment is believed to be marine macroalgae and microalgae [Tokarczyk and Moore, 1994; Sturges *et al.*, 1993; Nightingale *et al.*, 1995; Carpenter *et al.*, 2000] and that the production varies between algal species [Tokarczyk and Moore, 1994; Carpenter *et al.*, 2000], spatial and temporal variations in the concentrations of these compounds in seawater is not surprising. For example, marine microalgae are known to have patchy distributions [Levin and Segel, 1976; Mann and Lazier, 1996], and, particularly at higher latitudes, undergo complex seasonal cycles of productivity and species successions [e.g., Taylor *et al.*, 1993]: it thus follows that their products very likely have similar variability.

[4] Here we report seawater concentrations of CHBr_3 and CH_2Br_2 measured during two seasonal cycles (February 2005 to March 2007) at the Rothera Oceanographic and Biological Time Series (RaTS) site located in Marguerite Bay on the Antarctic Peninsula. The main aim of this study was to assess temporal variations in coastal bromocarbon concentrations in the waters of the Western Antarctic Peninsula.

2. Materials and Methods

2.1. Study Site

[5] All samples included in this study were collected at the RaTS site located in Ryder Bay at the northern end of Marguerite Bay (Figure 1), on the western coast of the Antarctic Peninsula. The main RaTS site (site 1) is located approximately 4 km offshore ($67^\circ 34.2'\text{S}$, $68^\circ 13.5'\text{W}$) to the east of Adelaide Island and has a water depth of 520 m. At times when this main site is not accessible because of ice cover, RaTS samples are taken at a second location (site 2) within Ryder Bay. Site 2 is at $67^\circ 34.9'\text{S}$, $68^\circ 9.3'\text{W}$ and has a water depth of 400 m. CTD transects indicate that there is full exchange between the waters of Ryder Bay and the larger expanse of Marguerite Bay. Data from in situ CTD loggers and observations of iceberg movement indicate tidal flushing of Ryder Bay and detailed comparison of the water column characteristics at the two RaTS sites indicate no

significant difference in water column structure or seasonal cycle, indicating that data from the two sites are fully comparable and representative of the regional picture [Clarke *et al.*, 2008]. Ice cover within Ryder Bay is highly variable with fast ice present for more than 200 days during some winters but only intermittent cover during other years [Clarke *et al.*, 2008]. The timing of the retreat of the ice during the summer months is also highly variable. Although this can occur in early November, during some years there may be extended periods of winter fast ice remaining within the bay until late December. Following the retreat of the winter fast ice there is an annual recurring phytoplankton bloom of large ($>20\text{ }\mu\text{m}$) diatoms within Ryder Bay during the summer, followed by a long winter period of very low chlorophyll *a* levels [Clarke *et al.*, 2008].

2.2. Sampling

[6] Samples were collected regularly for bromocarbon analysis between February 2005 and March 2007. However, particularly during the months of darkness, sampling frequency was constrained by weather conditions. The site was reached by small boat during periods of open water and by snowmobile when the winter fast ice was safe to traverse: during the winter, holes were cut in the ice to gain access to the water. Samples were collected from a Niskin bottle hand-winched to depth. As soon as the bottle was retrieved, subsamples were taken by gently filling amber glass-stoppered bottles using a piece of Tygon tubing. During our field season at Rothera (December to March 2005/2006) samples were collected from seven depths in the water column (0, 5, 10, 15, 25, 50, 100 m). At all other times samples were collected by the Rothera Marine Assistants (H. R. and P. M.) from 15 m (the reference depth for the RaTS work, and the long-term mean depth of the chlorophyll maximum in Ryder Bay).

[7] Following collection, aliquots were taken from the amber bottles in to a 100 ml glass syringe and gently filtered across a $0.7\text{ }\mu\text{m}$ filter (GF/F, Whatman) into a second syringe. At all times care was taken to avoid introduction of bubbles into the samples. Following filtration, a 40 ml sample was injected into a glass purge tube, where the bromocarbons were extracted by purging for 15 min using oxygen-free nitrogen (OFN) at a flow rate of 80 ml min^{-1} . Particles and water vapor were removed from the purge-gas stream using glass wool held in a section of glass tubing, and a counterflow Nafion dryer using OFN at a flow rate of 200 ml min^{-1} as the drying gas. The bromocarbons were then trapped and stored on Markes (Ltd) three-bed solid sorbent tubes containing Tenax, Carbograph and Carboxen. Between February 2005 and March 2006 only single or duplicate samples were collected from 15 m, but after March 2006 all samples were collected in triplicate. Depth profile samples were analyzed in duplicate. Air samples were collected in duplicate during the summer season 2006/2007 by drawing 1.5 to 2.0 L air through a sorbent tube using a glass syringe.

[8] During the summer 2005/2006, samples were analyzed using a gas chromatograph–mass spectrometer (see section 2.3) within 2–3 h. Since it was not possible to keep the instrument at the site long term, during other periods of sampling the Markes tubes were capped after purging,

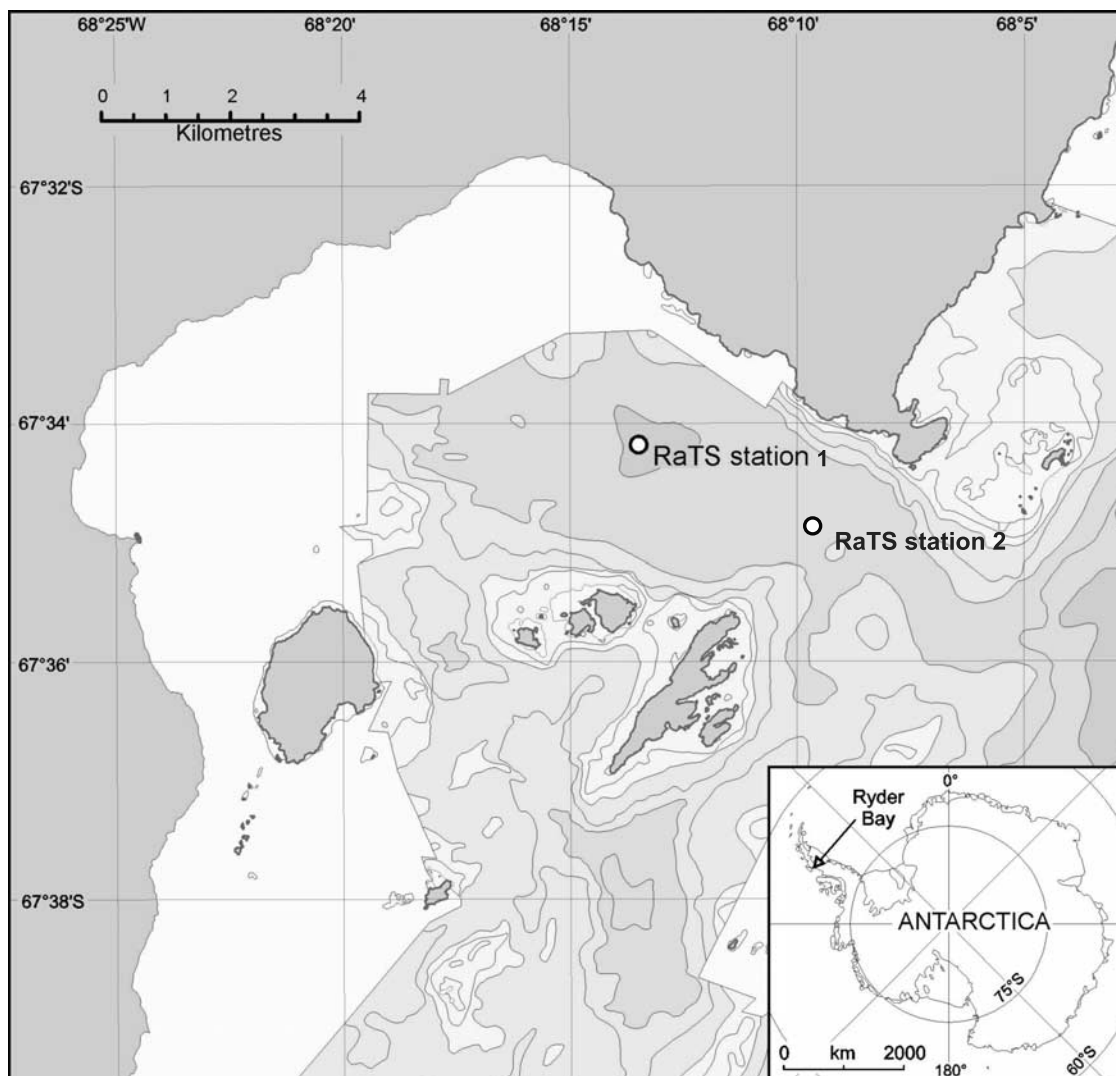


Figure 1. Map showing the location of the Rothera Oceanographic and Biological Time Series (RaTS) site.

stored at -20°C and returned to the University of East Anglia (UEA) for analysis 3–16 months after collection. Our storage tests show that there is no loss of CHBr_3 and CH_2Br_2 during long-term (i.e., <16 months) storage at this temperature. Storage tests were conducted as follows: toward the end of the summer season 2005/2006, 40 ml aliquots of the same seawater sample were purged on to six sorbent tubes, three tubes were analyzed immediately. The remaining three were stored at Rothera during subsequent site sampling (16 months) after which all tubes were returned to UEA for analysis. CHBr_3 and CH_2Br_2 concentrations in the test samples analyzed immediately were found to be $108.3 (\pm 13.5) \text{ pmol L}^{-1}$ and $13.5 (\pm 2.4) \text{ pmol L}^{-1}$, respectively. Stored test samples gave concentrations of $125.9 (\pm 20.0) \text{ pmol CHBr}_3 \text{ L}^{-1}$ and $14.5 (\pm 2.0) \text{ pmol CHBr}_3 \text{ L}^{-1}$, on the replicate sorbent tubes.

2.3. Bromocarbon Analysis

[9] Bromocarbon analysis was carried out using a semi-automated system comprising a Agilent gas chromato-

graph–mass spectrometer (GC-MS) coupled to a Markes Unity thermal desorption unit and Ultra autosampler. The GC was fitted with a 60-m capillary column (DB-VRX, J&W) and the MS operated in electron ionization (EI), single ion mode (SIM). Within the Unity the sorbent tubes were heated to 290°C and the desorbed gases were then refocused on a cold trap containing Tenax, Carbograph and Carboxen held at -10°C . The cold trap was then heated to 290°C and the desorbed bromocarbons introduced into the GC column using helium at a flow rate of 2 ml min^{-1} . Following the start of the GC run, the oven was held at 36°C for 5 min then heated up to 200°C at $20^{\circ}\text{C min}^{-1}$, held at 200°C for 2 min and then heated to 240°C at $40^{\circ}\text{C min}^{-1}$. The MS was configured to collect data between 6 and 18 min of the run. System calibrations were carried out using liquid standards (Sigma) gravimetrically prepared in HPLC-grade methanol (Fisher). Calibrations were carried out at regular intervals during the 2005/2006 summer season, and before and after batches of stored

Table 1. Details of the Data Used in the Bromocarbon Saturation Anomaly and Gas Flux Rate Calculations for the 2005/2006 and 2006/2007 Summer Seasons at the RaTS Site^a

| Summer Season | Seawater Data (m) | Atmospheric Mixing Ratio Data |
|---------------|-------------------|-------------------------------|
| 2005/2006 | 0 | 2006/2007 average measured |
| 2006/2007 | 15 ^b | |

^aRaTS, Rothera Oceanographic and Biological Time Series.^bMixed layer depth is ≥ 15 m.

samples were analyzed. Analytical detection limits were 0.3 pmol L^{-1} (seawater) and 0.1 ppt (air) for both CHBr_3 and CH_2Br_2 . Average percent analytical error (\pm standard deviation) calculated from sample replication was 2–18% for CHBr_3 and 1–23% for CH_2Br_2 .

2.4. Ancillary Parameters

[10] Size fractionated chlorophyll *a* concentrations were determined throughout the study period. This included $>20 \text{ }\mu\text{m}$ (microphytoplankton), $20\text{--}5 \text{ }\mu\text{m}$ (large nanophytoplankton), $5\text{--}2 \text{ }\mu\text{m}$ (small nanophytoplankton) and $2\text{--}0.2 \text{ }\mu\text{m}$ (picophytoplankton). The collection, preparation and analysis of the chlorophyll samples are described in detail by Clarke *et al.* [2008]. The level of ice cover within Ryder Bay was assessed visually by the Rothera Marine Assistant using an ice index (0–10). An ice index of 10 indicates total ice cover with fast ice, and 0 means open water. Intermediate scores indicate a combination of either incomplete fast ice cover, or the presence of other forms of ice (mainly pack ice or brash ice). Mixed layer depth was calculated using potential density.

2.5. Saturation Anomaly and Gas Flux Calculations

[11] Bromocarbon saturation anomalies were calculated for periods of open water when the seawater was free to exchange with the atmosphere. This parameter is defined as the percentage departure from the expected equilibrium between gas concentrations in surface seawater and the atmosphere. Thus, if a saturation anomaly is negative, a gas is entering the ocean from the atmosphere, and if it is positive the flux is from seawater into the atmosphere.

$$\text{Saturation anomaly}(\%) = 100 \times (\text{Cw} - \text{Ca}/H)/\text{Ca}/H$$

where *Cw* is the concentration in seawater, *Ca* is the concentration in air, and *H* is the dimensionless temperature-dependent Henry's Law coefficient, as reported by Moore *et al.* [1995] for CHBr_3 and CH_2Br_2 . Sea-air fluxes (*F*) were calculated using the gas flux parameterization (*k_w*) of Nightingale *et al.* [2000] using 7-day average (6 hourly) wind speed values recorded at the Rothera Research Station.

$$F = k_w \Delta C$$

where ΔC is the concentration difference across the sea-air interface. The temperature-dependent Schmidt number for CHBr_3 was calculated using the equations given by Quack and Wallace [2003]. Schmidt numbers for CH_2Br_2 were calculated using a combination of the diffusion coefficient equations given by Wilke and Chang [1955] and Hayduk

and Laudie [1974]. Simultaneous measurements of bromocarbon concentrations in surface waters and the atmosphere were not made consistently throughout this study. Consequently, 15-m water column concentrations and average bromocarbon mixing ratios are used in some calculations. The specific data used in the saturation anomaly and gas flux calculations for each summer season are detailed in Table 1. As no surface water bromocarbon data are available for the 2006/2007 summer, sea-to-air flux estimates for this season are only calculated when the mixed layer depth is ≥ 15 m.

3. Results and Discussion

3.1. Ancillary Parameters (15 m)

[12] Observed variations in chlorophyll *a* concentrations and sea-ice dynamics during the period in which the study was carried out (February 2005 to March 2007) were within the ranges of conditions seen in previous years. Figure 2a shows that periods of total sea-ice cover (index 10) occurred from early June until late December 2005, and from mid-June until mid-November 2006. The retreat of the sea ice thus occurred earlier in 2006 than in 2005.

[13] Consistent with previous years [Clarke *et al.*, 2008] peaks in chlorophyll *a* (Figure 2b), indicative of a microalgal bloom, were observed following the retreat of the sea ice during both summer seasons included in this time series. For the whole data set, the range of chlorophyll *a* concentrations during periods when fast ice was absent was $0.2\text{--}27.9 \text{ }\mu\text{g L}^{-1}$, compared to $0.1\text{--}0.7 \text{ }\mu\text{g L}^{-1}$ during the winter months with total ice cover. Seasonal ice edge blooms are a common feature of polar regions and are thought to be linked to the seeding of the pelagic population by ice algae and increased stability of the upper water column [Smith and Nelson, 1985], and the release of micronutrients such as iron to surface waters from ice melt [Sedwick and DiTullio, 1997]. The onset of the bloom at the end of 2005 is not well detailed because the condition of the sea ice and amount of brash ice did not permit passage to either sampling site. However, the relatively rapid retreat of the sea ice in 2006 allowed regular sampling and the onset of the bloom during this year coincided with the retreat of the ice and occurred around 10–15 November. Chlorophyll *a* concentrations were variable throughout both summer seasons yet both the average and maximum concentrations observed during the summer season 2005/2006 were higher than those measured during 2006/2007. During the first summer season, chlorophyll *a* concentrations peaked at $27.9 \text{ }\mu\text{g L}^{-1}$ with an average of $16.0 \text{ }\mu\text{g L}^{-1}$ between the onset of the bloom and the end of March 2006. For the 2006/2007 summer season, the maximum chlorophyll *a* concentration measured was $18.6 \text{ }\mu\text{g L}^{-1}$ with an average of $8.2 \text{ }\mu\text{g L}^{-1}$. Decreases in chlorophyll *a* concentrations down to winter values, indicating the end of the microalgal bloom, occurred during March in both years. As fast ice did not return to the bay until June this decrease was not driven by ice cover but was more likely linked to day length, nutrient availability or wind-driven turbulence.

[14] Size fractionated chlorophyll *a* data (Figure 2c) shows that the dominant microalgal group in the summer bloom in Ryder Bay consisted of large $>20 \text{ }\mu\text{m}$ microphytoplankton.

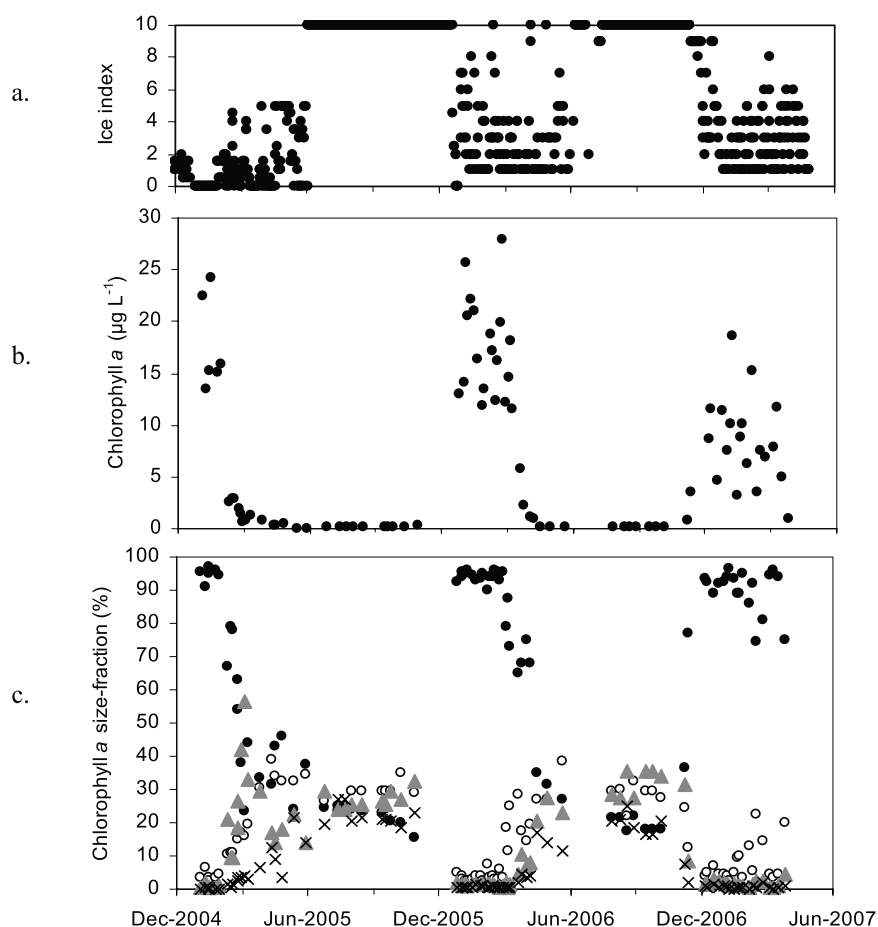


Figure 2. Observed variations in the (a) sea-ice index (0, open water; 10, total ice cover), (b) total chlorophyll *a* concentrations, and (c) size-fractionated chlorophyll *a* concentrations at the RaTS site (15-m depth) from February 2005 to March 2007. In Figure 2c, the closed circles represent $>20\ \mu\text{M}$ fraction, open circles represent $5\text{--}20\ \mu\text{M}$, gray triangles represent $2\text{--}5\ \mu\text{M}$, and crosses represent $0.2\text{--}2\ \mu\text{M}$.

Again, this is consistent with measurements from previous years [Clarke *et al.*, 2008]. The $>20\ \mu\text{m}$ fraction constituted $>60\%$ of the total chlorophyll *a* concentration during both summer seasons. However, contributions of the smaller ($<20\ \mu\text{m}$) nanophytoplankton and picophytoplankton were relatively more important during the winter when contributions from all fractions ($0.2\text{--}20\ \mu\text{m}$) are almost equal.

3.2. Seawater Bromocarbon Concentrations (15 m)

3.2.1. Seasonal Cycle

[15] Figure 3 shows the observed seasonal variations in seawater CHBr_3 and CH_2Br_2 concentrations at 15m depth at the RaTS site between February 2005 and March 2007. It is apparent from Figure 3 that there were distinct peaks in the seawater concentrations of both bromocarbons during the summer seasons of 2005/2006 and 2006/2007. Maximum CHBr_3 concentrations reached during the summer months were $254.2\ \text{pmol L}^{-1}$ in 2005/2006 and $276.4 (\pm 13.0)\ \text{pmol L}^{-1}$ in 2006/2007. The concentrations of CHBr_3 remained higher ($>100\ \text{pmol L}^{-1}$) for longer during the 2006/2007 summer than 2005/2006. For CH_2Br_2 the highest concentrations reached were $16.1\ \text{pmol L}^{-1}$ in the summer of 2005/2006 and $30.0 (\pm 0.4)\ \text{pmol L}^{-1}$ during

2006/2007. The relatively lower bromocarbon concentrations observed during the 2006/2005 summer can be explained by the occurrence of more high (7-day average) wind speeds (i.e., $>4\ \text{m s}^{-1}$) observed during this year (Figure 4). The model of Liss and Merlivat [1986] suggests that above approximately $4\ \text{m s}^{-1}$ the relationship between wind speed and sea-to-air gas exchange becomes steeper as manifested by increased waviness of the sea surface. In contrast to the summer values, the maximum bromocarbon concentrations measured under the winter fast ice were $39.5\ \text{pmol CHBr}_3\ \text{L}^{-1}$ and $9.6 (\pm 0.6)\ \text{pmol CH}_2\text{Br}_2\ \text{L}^{-1}$. The initial increase in CHBr_3 concentrations observed in Marguerite Bay was found to take place in late December in 2005 and mid-November in 2006, and coincided with the retreat of the sea ice and onset of the increase in chlorophyll *a* during both years. Peaks in CH_2Br_2 concentrations occurred slightly later than observed peaks in CHBr_3 . For example, during 2006/2007 maximum CHBr_3 concentrations were reached on 29 December (2006) but the highest CH_2Br_2 concentration was not measured until 31 January (2007).

[16] As was observed with chlorophyll *a* (Figure 2), decreases in bromocarbon concentrations down to winter values generally occurred before the return of the fast ice

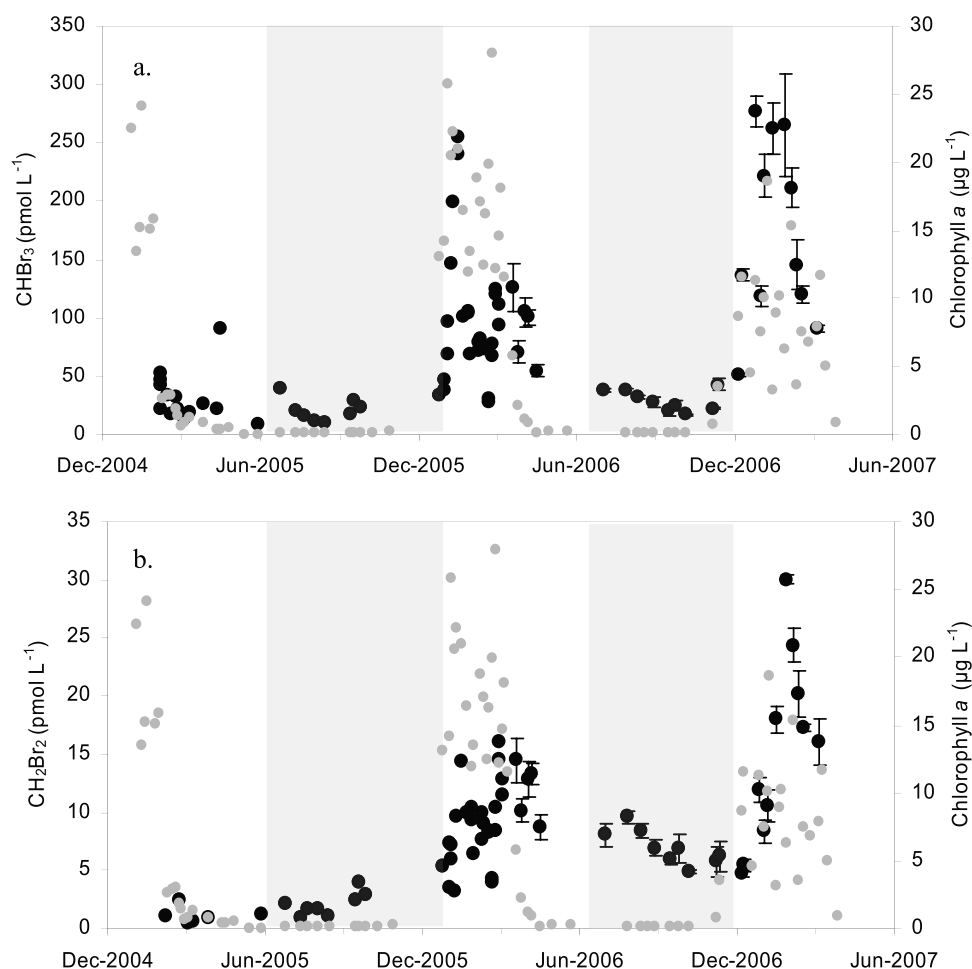


Figure 3. Observed variations in seawater (a) CHBr_3 and (b) CH_2Br_2 concentrations at the Time series RaTS site (15-m depth) from February 2005 to March 2007. Error bars are standard deviations of three replicate analyses. Variations in chlorophyll *a* are shown as gray closed circles for comparison. The gray shaded areas show the periods during which Marguerite Bay was covered by winter fast ice.

(Figure 3). The sea ice reformed in Marguerite Bay in May/June and retreated in early November in 2006 yet, despite the removal of sea-to-air flux as a loss process, decreases in bromocarbon concentrations were still observed under the ice during this year. For example, between 5 July and 9 October (2006) CHBr_3 concentrations decreased from $38.0 (\pm 1.0)$ to $17.0 (\pm 0.3)$ pmol L^{-1} and CH_2Br_2 concentrations decreased from $8.1 (\pm 1.0)$ to $5.0 (\pm 0.2)$ pmol L^{-1} . This is in contrast to the 2005 winter when, aside from a few high-concentration samples, bromocarbon concentrations remained relatively low and constant throughout.

3.2.2. Production and Loss Processes

[17] The seasonal cycles of CHBr_3 and CH_2Br_2 concentrations observed in Marguerite Bay are the result of temporal variations in the rates of production and loss within the water column. The main bromocarbon sources in seawater are believed to be marine macroalgae and microalgae [reviewed by Quack and Wallace, 2003], and previous studies have shown that these organisms produce CHBr_3 and CH_2Br_2 at very high rates [Carpenter *et al.*, 2000; Nightingale *et al.*, 1995; Laturnus, 1996]. As iceberg scouring means that the seaweed populations in Marguerite

Bay are very limited and restricted in distributions, macroalgae are unlikely to be a major contributor to the bromocarbon inventory of the study region. This, together with the coincidence of the increased bromocarbon concentrations with the high chlorophyll *a* concentrations during the summer months, suggests that microalgae are the major source of CHBr_3 and CH_2Br_2 in Marguerite Bay. Previous studies have demonstrated CHBr_3 and CH_2Br_2 production by large polar diatoms, which are likely to be a major component of the $>20 \mu\text{M}$ phytoplankton that size-fractionated chlorophyll *a* data suggest dominate the Marguerite Bay microalgal bloom (see Figure 2). For example, Tokarczyk and Moore [1994] and Moore *et al.* [1996] present results from laboratory culture studies of cold water diatoms which show that species of the commonly occurring genera *Nitzschia* and *Porosira* produce CHBr_3 and CH_2Br_2 . Additionally, Sturges *et al.* [1993] have shown that ice algae, collected from the underside of sea ice in McMurdo Sound, Antarctica produce both CHBr_3 and CH_2Br_2 . The occurrence of the peak in CH_2Br_2 concentrations after that of CHBr_3 could be due to an alteration of the ratio of production of the two compounds as the bloom progresses, or it is possible that there is some

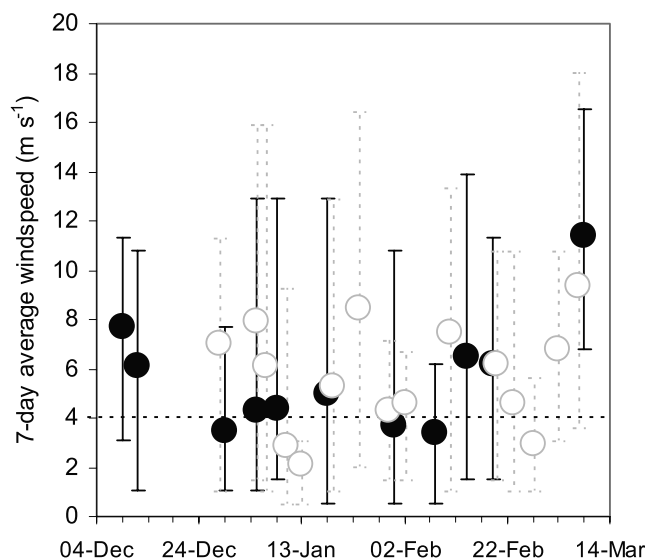


Figure 4. Average wind speeds calculated for the 7-day period prior to collection of each seawater sample at the RaTS site for the 2005/2006 (open gray circles) and 2006/2007 (closed black circles) summers. Range bars show the minimum and maximum values. The dashed line highlights 4 m s^{-1} , which is the level at which the model of Liss and Merlivat [1986] suggests that the relationship between wind speed and sea-to-air gas exchange steepens.

conversion of CHBr_3 to CH_2Br_2 via reductive dehalogenation [Tanhua et al., 1996; Quack et al., 2007].

[18] To investigate if microalgae are likely to be the bromocarbon source at 15 m in Marguerite Bay, we compare our observed rates of increase in concentrations to those reported for cultures of polar diatoms [Tokarczyk and Moore, 1994]. Net rates of change of CHBr_3 and CH_2Br_2 concentrations were calculated stepwise for the period immediately following the retreat of the ice during which chlorophyll *a* concentrations were increasing (4–13 January 2005; 9–29 December 2006). The resulting rates of change in CHBr_3 and CH_2Br_2 concentrations were -26 to $29 \text{ pmol L}^{-1} \text{ d}^{-1}$ and -1 to $1 \text{ pmol L}^{-1} \text{ d}^{-1}$, respectively. When these are normalized to chlorophyll *a* they yield maximum rates of increase of $60 \text{ nmol CHBr}_3 (\text{g chl } a)^{-1} \text{ h}^{-1}$ and $6 \text{ nmol CH}_2\text{Br}_2 (\text{g chl } a)^{-1} \text{ h}^{-1}$ which are similar to the production rates (30 to $72 \text{ nmol CHBr}_3 [\text{g chl } a]^{-1} \text{ h}^{-1}$; 4 to $5 \text{ nmol CH}_2\text{Br}_2 [\text{g chl } a]^{-1} \text{ h}^{-1}$) observed by Tokarczyk and Moore [1994] in laboratory cultures of cold water diatoms. The production rates calculated for Marguerite Bay are net rates of increase and gross production rates may be higher when in situ losses are accounted for. However, the mixed layer depth was shallower than 15 m for most of period for which these calculations were made so the bromocarbons at this depth would not have been subject to sea-to-air gas exchange, which is believed to be the major loss process for these compounds from surface seawater [Carpenter and Liss, 2000; Quack and Wallace, 2003]. Therefore, these comparable field and laboratory production rates suggest that microalgae are indeed capable of producing CHBr_3 and

CH_2Br_2 at the rates these compounds were found to increase in Marguerite Bay. Many previous measurements of bromocarbon concentrations at levels similar to those determined in Marguerite Bay (e.g., up to $276.4 \pm 13.0 \text{ pmol CHBr}_3 \text{ L}^{-1}$) are from areas influenced by large seaweed populations. For example, equally high CHBr_3 concentrations have been observed around Svalbad [Fogelqvist, 1985], off the coast of Nova Scotia [Moore and Tokarczyk, 1993], in waters around Mace Head, Ireland [Carpenter and Liss, 2000], and on the western coast of Scotland [Nightingale et al., 1995]. The general conclusion from these studies is that macroalgae are the major contributors to the bromocarbon inventory of the study regions. However, our results suggest that, especially in polar regions, coastal microalgae could also make an important contribution.

[19] Despite the similarity in the production rates observed here in the field and by Tokarczyk and Moore [1994] in microalgal cultures, there are no strong correlations between chlorophyll *a* and CHBr_3 or CH_2Br_2 concentrations, either for the whole data set ($R^2 < 0.30$) or for the individual summer seasons ($R^2 < 0.40$) but this is not surprising for several reasons. For example, although chlorophyll *a* is found in all microalgae, studies have shown that there are variations in the bromocarbon production rate between different microalgal species [Tokarczyk and Moore, 1994; Moore et al., 1996]. There may be one microalgal species within a mixed population which dominates bromocarbon production in Ryder Bay. Additionally, although wind-driven mixing will impact both the bromocarbon concentrations, through sea-to-air gas exchange and dilution, and the phytoplankton population, through enhanced turbulence [Lewis et al., 1984], the relative influence of these will not be constant.

[20] The decreasing bromocarbon concentrations observed at 15 m in Marguerite Bay toward the end of the summer seasons will have been due to a change in the relative importance of the production and loss terms. First, these lower bromocarbon concentrations are likely in line with decreased production rates associated with the seasonal decline in biological activity, expected at higher latitudes. This is evidenced by the decrease in chlorophyll *a* (Figure 2) toward the end of the summer. Second, losses due to sea-to-air gas exchange and dilution would have been enhanced toward the end of both summer seasons because of the pronounced deepening of the mixed layer depth which takes place at this time (Figure 5). The continued decline in bromocarbon concentrations measured under the ice in 2006 suggests that sea-to-air gas exchange is not the only loss process for CHBr_3 and CH_2Br_2 in seawater. Episodic flushing of Marguerite Bay by circumpolar current water [Clarke et al., 2008] and downward mixing would result in a decline in bromocarbon concentrations. Results from previous studies suggest that CH_2Br_2 is degraded by marine bacteria [Goodwin et al., 1997], and there may also be rapid biological loss processes for CHBr_3 [Quack et al., 2007], which could additionally be responsible for the observed decrease in the concentrations of the compounds.

3.2.3. Bromocarbon Concentration Ratio

[21] Previous studies have shown that CHBr_3 and CH_2Br_2 concentrations in seawater and the marine atmosphere are

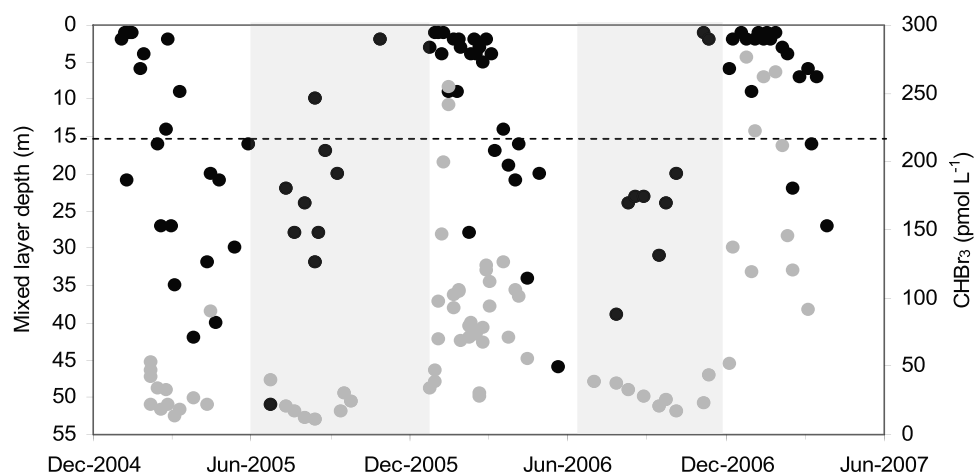


Figure 5. Variations in mixed layer depth (closed black circles) at the RaTS site between December 2004 and June 2007. The dashed line highlights 15 m which is the depth at which samples for bromocarbon analysis were collected throughout the study period. CHBr_3 concentrations (gray closed circles) at 15-m depth are also shown for comparison. The gray shaded areas show the periods during which Marguerite Bay was covered by winter fast ice.

well correlated suggesting a common source [Schall and Heumann, 1993; Carpenter and Liss, 2000]. Figure 6 shows a plot of CHBr_3 against CH_2Br_2 concentrations in seawater for the whole data set collected during this study. The overall correlation between CHBr_3 and CH_2Br_2 concentrations is low ($R^2 = 0.58$, $p < 0.001$, $n = 66$) relative to values from previous studies. For example, Schall and Heumann [1993] found CH_2Br_2 and CHBr_3 concentrations in seawater samples collected around Spitzbergen to correlate with an R^2 of 0.90. However, when the Marguerite Bay data are divided into temporal subsets the correlations are stronger and different relationships between the two gases emerge. Laboratory culture studies suggest that the rate of bromocarbon production is higher when microalgal biomass is increasing [Tokarczyk and Moore, 1994] so the data collected during ice-free periods were divided into two groups on the basis of the chlorophyll *a* data. Group 1 includes samples collected after the retreat of the ice, when chlorophyll *a* concentrations were increasing, and group 2 includes data collected later in the summer. The correlation coefficients obtained for groups 1 and 2 are higher (group 1, $R^2 = 0.64$, $p < 0.001$, $n = 12$ and group 2, $R^2 = 0.89$, $p < 0.001$, $n = 38$) than the overall value. Additionally, the slopes of the regression lines are different for the two groups (group 1 = 0.04 and group 2 = 0.11) indicating relatively higher CHBr_3 in early summer. Also shown in Figure 6 are the regression lines for the 2005 and 2006 periods of ice cover, which we treat separately since the data appear to form two distinct subsets. There are highly significant correlations of CHBr_3 and CH_2Br_2 concentrations within these subsets (2005: $R^2 = 0.95$, $p < 0.001$, $n = 8$; 2006: $R^2 = 0.89$, $p < 0.001$, $n = 8$) with slopes of 0.13 and 0.19 for the 2005 and 2006 winters, respectively.

[22] This analysis of our long-term seawater bromocarbon concentration data indicates that seasonality is an important factor in the relationship between CH_2Br_2 and CHBr_3 and

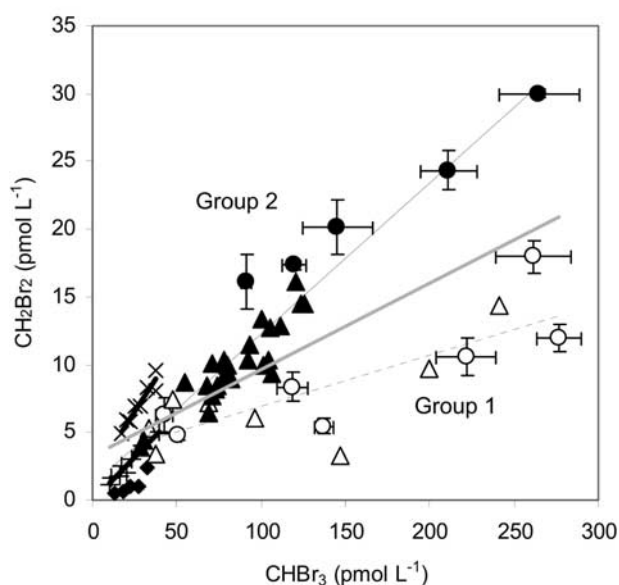


Figure 6. Correlations of seawater CHBr_3 and CH_2Br_2 concentrations collected from February 2005 to March 2007 at the RaTS site (15-m depth). Open symbols indicate samples taken when chlorophyll *a* concentrations were increasing (group 1: open triangles, 2005/2006 summer; open circles, 2006/2007 summer), closed symbols show other ice-free periods (group 2: closed diamonds, summer 2005; closed triangles, summer 2006; closed circles, summer 2007), and crosses indicate samples taken under the winter fast ice (+, 2005 winter; x, 2006 winter). The least squares regression lines are as follows: all data (gray line, $R^2 = 0.58$, $p < 0.001$, $n = 66$); group 1 (black dashed line, $R^2 = 0.64$, $p < 0.001$, $n = 12$); group 2 (black continuous line, $R^2 = 0.89$, $p < 0.001$, $n = 38$); 2005 winter (lower bold line, $R^2 = 0.95$, $p < 0.001$, $n = 8$); and 2006 winters (upper bold line, $R^2 = 0.89$, $p < 0.001$, $n = 8$). Error bars show standard deviations.

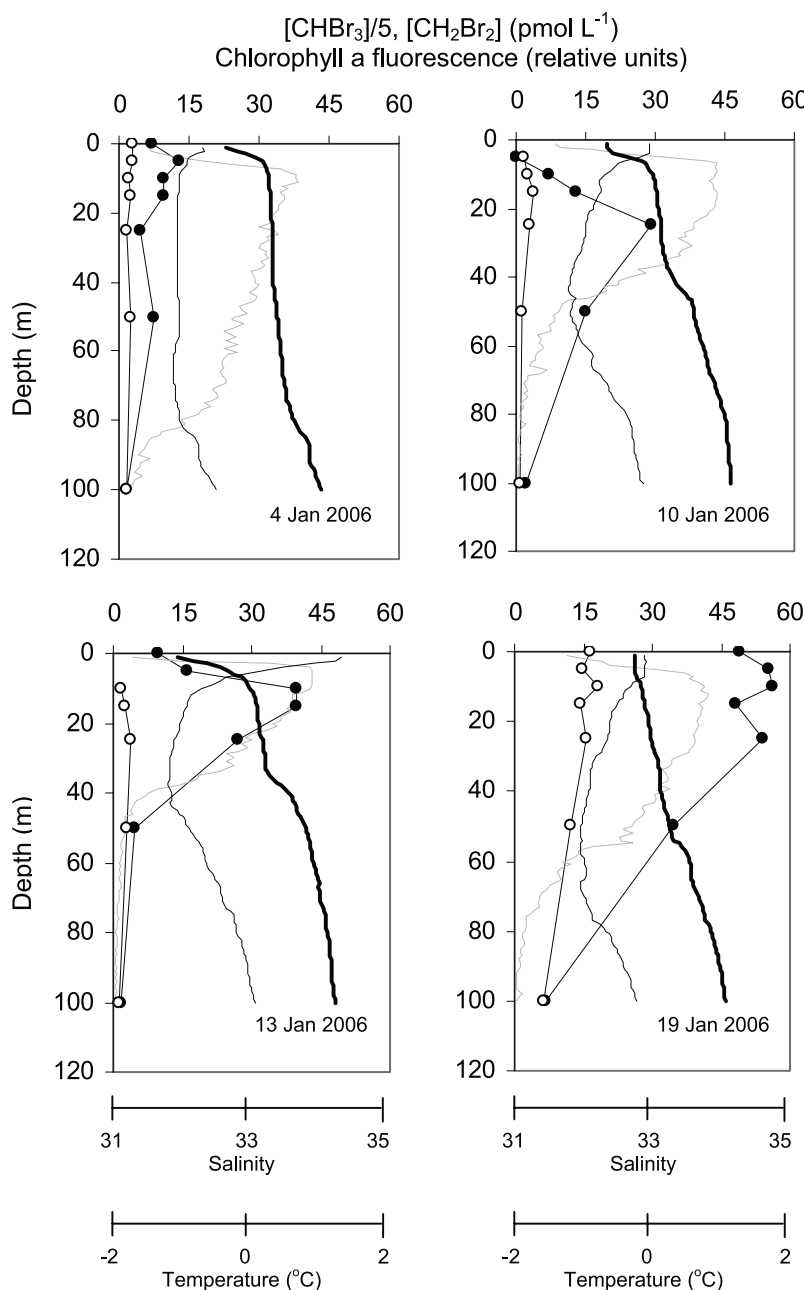


Figure 7. Depth profiles of CHBr_3 (closed circles) and CH_2Br_2 (open circles) collected at the RaTS site between 4 and 19 January 2006. Also shown are chlorophyll *a* fluorescence (gray line), potential temperature (thin black line), and salinity (bold black line).

this may be true for other higher-latitude regimes. The different slopes of the relationships between CH_2Br_2 and CHBr_3 obtained for group 1 (0.04) compared to group 2 (0.11), and underice concentrations (0.13–0.19) suggest that $\text{CH}_2\text{Br}_2/\text{CHBr}_3$ is lower close to the source regions which is consistent with the conclusions of *Carpenter and Liss* [2000]. A greater understanding of the processes controlling the concentrations of both gases is required before the $\text{CH}_2\text{Br}_2/\text{CHBr}_3$ can be utilized to resolve when and where bromocarbon production is taking place, but our

results suggest that it would be worthwhile exploring the factors influencing this relationship.

3.2.4. Bromocarbon Depth Profiles

[23] Figure 7 shows four depth profiles of CHBr_3 and CH_2Br_2 collected during the early stages of the microalgal bloom in Marguerite Bay between 4 and 19 January (2006) in the upper 100 m of the water column. The overall depth distributions of CHBr_3 and CH_2Br_2 are consistent with previous observations [reviewed by *Quack and Wallace*, 2003] with the higher concentrations in the upper water

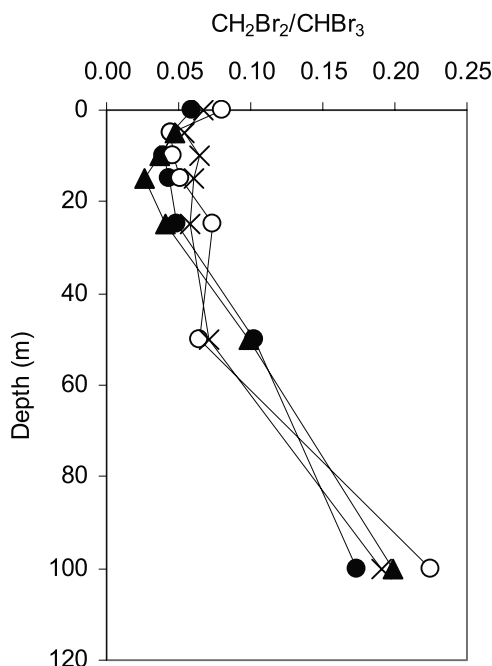


Figure 8. Depth profiles of $\text{CH}_2\text{Br}_2/\text{CHBr}_3$ measured during 2006 on 4 (open circles), 10 (triangles), 13 (closed circles), and 19 January (crosses) for samples collected at the RaTS site.

column suggestive of a biological source. To support this, water column profiles of bromocarbon concentrations and chlorophyll *a* fluorescence are similar in all 4 plots. When there are fairly distinct subsurface peaks in chlorophyll *a* fluorescence (10 and 13 January) these are associated with peaks in CHBr_3 and CH_2Br_2 concentrations. However, when chlorophyll *a* fluorescence is more homogeneous in the water column the bromocarbons are also more evenly distributed. Examination of the relationship between the two gases in these four depth profiles shows that $\text{CH}_2\text{Br}_2/\text{CHBr}_3$ is generally lower in the upper water column (Figure 8). This is supportive of the suggestions made in section 3.2.3 that $\text{CH}_2\text{Br}_2/\text{CHBr}_3$ is lower where active production is taking place. The slight increase in ratio at the surface observed in all profiles could be due to sea-to-air gas exchange as the higher-concentration difference across the sea surface for CHBr_3 would drive increased fluxes of this gas compared to CH_2Br_2 .

[24] *Carpenter et al.* [2007] show that the highest CHBr_3 concentrations they observed in the Southern Ocean are associated with waters influenced by ice melt, and use this to suggest a potential link with ice algae. To investigate if this holds true for the data collected in this study, potential temperature/salinity (T/S) characteristics were compared to CHBr_3 concentrations measured in the depth profiles collected on 4, 10, 13, and 19 January (Figure 9). The water masses in Marguerite Bay have been well characterized [*Clarke et al.*, 2008] and consist of upper circumpolar deep water (UCDW), winter water (WW), and a relatively warm and fresh surface layer which forms in the summer. The v-shaped inflection of the T/S plots is typical of data from the austral summer and is due to the temperature minimum

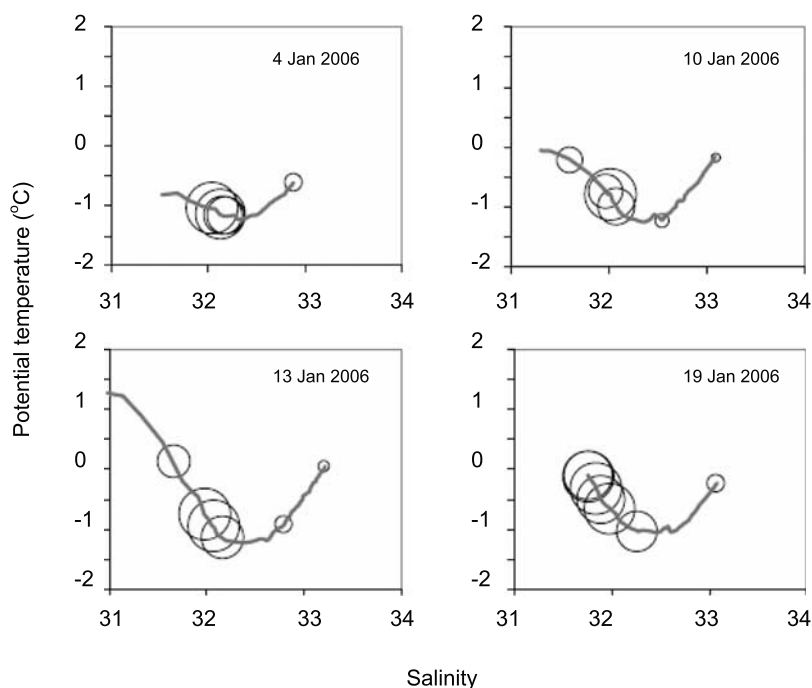


Figure 9. Potential temperature/salinity characteristics of the upper 100 m at the RaTS site for depth profiles taken on 4, 10, 13, and 19 January 2006 (bold gray line). CHBr_3 concentrations at each depth are proportional to the area of the open circles.

Table 2. Bromocarbon Atmospheric Mixing Ratios Observed at the RaTS Site in Marguerite Bay During the 2006/2007 Summer Season^a

| Date | Atmospheric Mixing Ratio (ppt) | |
|-------------|--------------------------------|---------------------------------|
| | CHBr ₃ | CH ₂ Br ₂ |
| 10 Nov 06 | 0.5–0.8 | 0.3–0.4 |
| 15 Nov 06 | 1.0–1.4 | 0.3–0.4 |
| 09 Dec 06 | 1.7–2.2 | 0.3–0.4 |
| 12 Dec 2006 | 0.8–0.9 | 0.2–0.3 |
| 29 Dec 2006 | 2.7–2.8 | 0.4 |
| 4 Jan 2007 | 1.9–2.5 | 0.3–0.4 |
| 8 Jan 2007 | 1.4–1.5 | - |
| 18 Jan 2007 | 3.0–4.1 | 0.4–0.5 |
| 31 Jan 2007 | 7.3–7.5 | 0.5–0.6 |
| 8 Feb 2007 | 5.3–5.7 | 0.7 |
| 19 Feb 2007 | 2.2–2.4 | 0.4 |
| 9 Mar 2007 | 1.9–2.0 | 0.4 |

^aThe range of values shows the two mixing ratios obtained from duplicate samples. Where only one value is given, both duplicates gave the same concentration.

of WW [Clarke *et al.*, 2008]. UCDW is characterized by relatively high salinities (≥ 34.5) and temperature ($\sim 1^\circ\text{C}$) so the T/S plots confirm that none of the bromocarbon samples included in this study were taken within this water mass. However, measurements were made in the waters resulting from the mixing of UCDW and WW ($< -1^\circ\text{C}$) but the concentrations of both CHBr₃ and CH₂Br₂ were found to be relatively low within these samples. In all profiles, the highest bromocarbon concentrations were found in the relatively fresh and warm surface layer that forms because of a combination of ice melt and surface heating during the summer months. Consequently, as was observed by Carpenter *et al.* [2007], the highest bromocarbon concentrations are associated with waters influenced by ice melt which could suggest a link with ice algae, or indicate that CHBr₃ and CH₂Br₂ are released from brine channels. The relatively low bromocarbon concentrations observed on 10 and 13 January in the warmest and freshest waters could be the result of a higher rate of sea-to-air gas exchange at the surface. T/S characteristics for 13 and 19 January suggest that between these dates warmer surface waters were mixed with cooler deeper waters because of deeper mixing, and this resulted in the bromocarbon concentrations becoming more homogenous in the upper 50 m of the water column. The resulting increase in CHBr₃ and CH₂Br₂ concentrations at the surface would drive higher sea-to-air fluxes of these compounds.

3.3. Atmospheric Concentrations, Saturation Anomalies, and Gas Flux Calculations

[25] Atmospheric mixing ratios of CHBr₃ and CH₂Br₂ measured at the RaTS site during the summer 2006/2007 are given in Table 2. Average values measured in Marguerite Bay were found to be 2.7 ppt ($n = 12$; range = 0.5–7.5 ppt) for CHBr₃ and 0.4 ppt ($n = 11$; range = 0.3–0.7 ppt) for CH₂Br₂. Carpenter *et al.* [2007] recently measured a mean atmospheric mixing ratio of 0.9 ppt CHBr₃ above the Southern Ocean which is similar to the lowest value that we measured for this compound but higher CHBr₃ mixing

ratios have been measured in Antarctica. For example, Reifenhauer and Heumann [1992] found that atmospheric CHBr₃ mixing ratios in air over Antarctica can range from 1.0 to 37.4 ppt. The lowest CHBr₃ mixing ratios observed here and by Reifenhauer and Heumann [1992] (~ 1.0 ppt) have been suggested to be indicative of clean marine air [Quack and Wallace, 2003].

[26] A summary of the calculated saturation anomalies and gas flux rates for both summer seasons are given in Table 3. The range of calculated saturation anomalies were found to be -50 to 637% for CHBr₃ and 7 – 313% for CH₂Br₂. Average bromocarbon sea-to-air flux rates from Marguerite Bay were 84 (-13 to 275) $\text{nmol CHBr}_3 \text{ m}^{-2} \text{ d}^{-1}$, and 21 (2 – 70) $\text{nmol CH}_2\text{Br}_2 \text{ m}^{-2} \text{ d}^{-1}$. The average CHBr₃ flux rate reported by Carpenter *et al.* [2007] for another coastal area of Antarctica is $32 \text{ nmol m}^{-2} \text{ d}^{-1}$, which is within the range of values we report. However, the maximum flux reported by Carpenter *et al.* [2007] is $101 \text{ nmol CHBr}_3 \text{ m}^{-2} \text{ d}^{-1}$ whereas we calculate fluxes of this compound up to $275 \text{ nmol m}^{-2} \text{ d}^{-1}$. The lower chlorophyll *a* waters studied by Carpenter *et al.* [2007] may thus represent a smaller source of bromine to the atmosphere at certain periods during the austral summer. Estimates for more open ocean areas of the Southern Ocean yield much lower flux rates than reported here and by Carpenter *et al.* [2007]. For example, from a review of the literature, Quack and Wallace [2003] calculate an average sea-to-air CHBr₃ flux of $3 \text{ nmol m}^{-2} \text{ d}^{-1}$ for open ocean areas between 50 and 80°S . Additionally, Chuck *et al.* [2005] found offshore areas of the Southern Ocean (50 – 65°S) to be undersaturated with respect to CHBr₃, suggesting that the net flux of this compound would be from the atmosphere in to the ocean. This comparison of our flux estimates with those reported previously in the literature suggests that bromocarbon fluxes from the Southern Ocean are spatially heterogeneous.

3.4. Implications for Sea-to-Air Bromine Flux From the Antarctic Peninsula

[27] Assuming all of the bromine that is carried across the sea surface as CHBr₃ and CH₂Br₂ is released to the atmosphere because of photolysis, the average bromocarbon flux rates we report for Marguerite Bay would result in a rate of transfer of approximately $2 \times 10^8 \text{ atoms Br cm}^{-2} \text{ s}^{-1}$ to the Antarctic atmosphere. These fluxes are of the same order as those (6×10^7 – $1 \times 10^8 \text{ atoms Br cm}^{-2} \text{ s}^{-1}$) which von Glasow *et al.* [2004] suggest are required to maintain ppt levels of tropospheric bromine which would contribute significantly to tropospheric ozone depletion. Determining

Table 3. Ranges of Calculated CHBr₃ and CH₂Br₂ Saturation Anomalies and Gas Flux Rates for the RaTS Site in Marguerite Bay for Two Summer Seasons^a

| Summer | Saturation Anomaly (%) | | Flux Rate ($\text{nmol m}^{-2} \text{ d}^{-1}$) | |
|-----------|------------------------|---------------------------------|---|---------------------------------|
| | CHBr ₃ | CH ₂ Br ₂ | CHBr ₃ | CH ₂ Br ₂ |
| 2005/2006 | -50 – 637 | 7 – 295 | -13 – 226 | 2 – 28 |
| 2006/2007 | 97 – 233 | 233 – 313 | 230 – 275 | 64 – 70 |

^aSeasons are 2005/2006 and 2006/2007.

the exact significance of the sea-to-air bromine fluxes we estimate for Marguerite Bay is difficult without their incorporation in to an atmospheric chemistry model. However, seasonal ice edge blooms such as that we studied in Marguerite Bay occur annually during the summer months over large areas of the Southern Ocean [Garibotti *et al.*, 2005]. Consequently, if the levels of bromocarbon concentrations and sea-to-air fluxes we present for the RaTS site are representative of blooms occurring elsewhere, emissions of CHBr_3 and CH_2Br_2 during the summer months could have an important influence on the chemistry and composition of the Antarctic atmosphere.

4. Conclusions

[28] This study has shown that there is strong seasonality in seawater bromocarbon concentrations and emissions to the atmosphere from Marguerite Bay on the western Antarctic Peninsula. Compared to the winter values, during the summer microalgal bloom the seawater concentrations of CHBr_3 and CH_2Br_2 were found to increase significantly by a factor of 10 and 3, respectively. Additionally, a comparison of our results with those published previously in the literature for more open ocean areas of the Southern Ocean [Quack and Wallace, 2003; Chuck *et al.*, 2005] suggest that coastal areas are hot spots of bromocarbon production and fluxes to the Antarctic atmosphere. Spatial and temporal variability in sea-to-air bromocarbon emissions is not yet incorporated into models of atmospheric bromine chemistry [e.g., von Glasow *et al.*, 2004]. The results presented here suggest that the current practice of assuming a spatially and temporally homogeneous emission rate of CHBr_3 and CH_2Br_2 may lead to inaccuracies in model outputs by underestimating the importance of local emissions. Our results suggest that the timing of sea-ice retreat plays a major role in controlling when sea-to-air bromocarbon emissions occur. The Antarctic Peninsula is presently experiencing rapid climate change [Clarke *et al.*, 2007] which is expected to result in a modification of sea-ice dynamics which could alter the timing, species composition and duration of the microalgal bloom in this area. If this occurs, future changes in bromocarbon production in the seasonal ice edge zone seem likely. Consequently, a greater understanding of what controls bromocarbon production in this area, together with further long-term monitoring are required to assess the importance of current emissions and how sea-to-air bromine fluxes will alter with future environmental change.

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